PCT WORLD INTELLECTU/ Intern

INTERNATIONAL APPLICATION PUBLISHED I

WO 9602317A1

(51) International Patent Classification 6 : B01D 71/10, 71/14, 69/10 | A1

(11) International Publication Number: WO 96/02317

(43) International Publication Date: 1 February 1996 (01.02.96)

(21) International Application Number: PCT/US95/09836

(22) International Filing Date: 19 July 1995 (19.07.95)

(30) Priority Data:
08/277,806 20 July 1994 (20.07.94) US

(71) Applicant: MILLIPORE CORPORATION [US/US]; 80 Ashby Road, Bedford, MA 01730 (US).

(72) Inventors: TUCCELLI, Ronald; 56 Highland Avenue, Winchester, MA 01890 (US). MCGRATH, Paul, V.; 30 Crescent Avenue, Bedford, MA 01730 (US).

(74) Agent: KARNAKIS, Andrew, T.; Millipore Corporation, 80 Ashby Road, Bedford, MA 01730 (US).

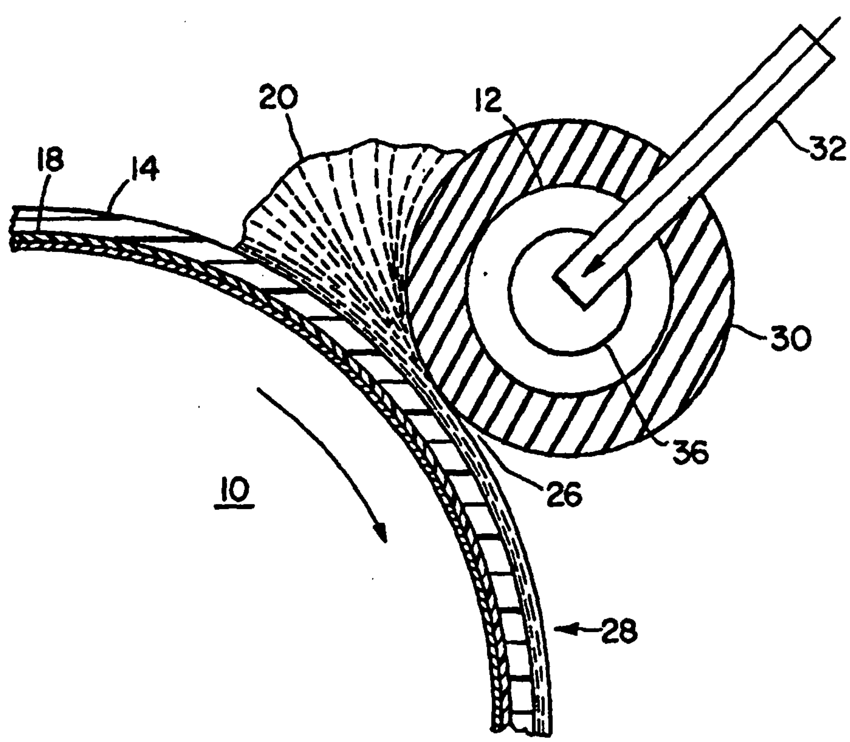
(81) Designated States: CN, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: CELLULOSIC ULTRAFILTRATION MEMBRANE

(57) Abstract

A cellulosic ultrafiltration membrane is provided having a microporous base resistant substrate and an ultrafiltration layer form of a cellulose ester or cellulose.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

CELLULOSIC ULTRAFILTRATION MEMBRANE

BACKGROUND OF THE INVENTION

This invention relates to high strength ultrafiltration membranes and to a process for producing such membranes. More particularly, this invention relates to high strength cellulosic ultrafiltration membranes made from a microporous polymeric base-resistant substrate and a thin cellulose or cellulose ester polymer ultrafiltration layer.

Microporous and open ultrafiltration membranes include thin sheets and hollow fibers generally formed from polymeric material and having a substantially continuous matrix structure containing open pores or conduits of small size. The pore size range for pores of microporous membranes are generally understood to extend from about 0.05 microns to about 10 microns. Composite ultrafiltration (UF) membranes are UF membranes formed on a pre-existing microporous membrane substrate. The composite membranes have better integrity (higher bubble points) than UF membranes cast from the same polymer solutions onto traditional non-woven backing materials such as a non-woven polyester substrate. For example, U. S. Patent 4,824,568 discloses high bubble point membranes that are composites of polyvinylidene fluoride (PVDF) or polyethersulfone solutions coated onto a 0.22 micron PVDF microporous substrate. The PVDF solutions are based on solvents that also soften a portion of the PVDF substrate. It is presently believed that this solvent bonding is necessary in order to prevent delamination of the composite structure. However, European Patent Application number 93,117 495.7 having publication number 0596411A2 teaches that the use of such a solvent system is undesirable since it can soften the microporous substrate. The use of PVDF also is disadvantageous since PVDF is attacked by common cleaning and sanitizing agents such as 0.5N NaOH. These PVDF based composites, therefore, are not

appropriate for use in process streams that foul membranes such as serums, fermentation broths or other protein separation processes which then must be cleaned and sanitized by NaOH.

At the present time, ultrafiltration membranes comprised of cellulose are used in applications where low protein binding and low fouling characteristics are required. Cellulose ultrafiltration membranes are formed by immersion casting of a cellulose acetate polymer solution onto a non-woven fabric substrate formed, for example, from polyethylene or polypropylene. The non-woven substrate has relatively large pores, typically in the order of several hundred microns in effective diameter in comparison to the UF layer formed on it. The UF layer is typically bound to some degree to the substrate by mechanical interlocking of the UF layer and the substrate. The cellulose acetate is then hydrolyzed to cellulose by using a strong base such as 0.5N NaOH.

Alternatively, cellulose can be dissolved in solutions of solvents such as dimethylacetamide (DMAC) or N-methyl pyrrolidone (NMP) with the addition of a salt such as lithium chloride. This cellulose solution can be used to form the composite membrane and subsequently eliminate the need for base hydrolysis.

While these composite membranes are considered to be generally satisfactory, they are not considered to be defect free. A defect is an area of the membrane where a void or rupture in the UF layer will allow passage of particles significantly larger than the retention limit dictated by the UF layer. These defects can result from fibers of the non-woven substrate extending though the UF layer or from gas bubbles retained in the solution from which the cellulose acetate layer is precipitated and coagulated which rupture the UF layer. In addition, defects are caused by the relatively high variability of the non-woven substrate thickness which increases the difficulty of achieving a uniformly thick UF layer. The resultant

variable UF layer thickness results in variable permeability and retention performance.

Presently available cellulosic membranes have an undesirably low mechanical strength in that they are easily ruptured when subjected even to low back pressure or when folded even to a minor degree. Delamination of presently available cellulosic membranes is commonly observed at low back pressures of about 3 to 15 psi. Since such membranes can be exposed to some back-pressure during use, resistance to delamination under such back-pressure conditions is desirable.

Accordingly, it would be desirable to provide a cellulosic ultrafiltration membrane which is free of defects, exhibits low protein binding, is stable in high pH solutions, is highly resistant to high back pressure and is mechanically stable even when folded. Such a composite membrane could be highly useful for processing protein-containing solutions under conditions of repeated use. It would also maintain membrane integrity while under conditions of pressure normally encountered during use.

SUMMARY OF THE INVENTION

The present invention provides a defect free cellulosic ultrafiltration membrane formed from a microporous polymeric substrate which is resistant to high pH (base) conditions and a cellulose ester or cellulose ultrafiltration layer. The thickness of the ultrafiltration layer is controlled so that it is rendered defect free. The degree of penetration of the cellulose ester or cellulose into the base resistant microporous polymeric layer is controlled so as to prevent excessive plugging of the substrate pores thereby to maintain desirable flux characteristics for the cellulosic membrane. The degree of penetration of the cellulose ester or cellulose into the base resistant polymeric microporous layer is also controlled to obtain a sufficiently

strong bond between the two layers. This renders the cellulosic membrane highly resistant to delamination.

The cellulosic ultrafiltration membrane of this invention can be formed by passing a base resistant polymeric microporous substrate and a solution of cellulose or a cellulose ester into a nip formed by (a) a rubber roll with or without a film thereon and (b) a rotating cylinder. The thickness of the ultrafiltration layer and the degree of penetration of the ultrafiltration layer into the microporous layer is controlled by the pressure at the nip, the durometer (hardness) and diameter of the rubber roll, solution viscosity and process speed. Optionally, the cellulose or cellulose ester solution can be applied to the base resistant microporous polymeric substrate by a conventional knife-over-roll or slot die coating methods. The coated microporous substrate is then contacted with a non-solvent for the cellulose or cellulose ester to effect its precipitation to form the ultrafiltration layer. The cellulose ester can be converted to cellulose by reaction with a base such as NaOH.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 illustrates an apparatus suitable for forming the composite ultrafiltration membrane of this invention.

Fig. 1A illustrates an alternative apparatus suitable for forming the composite ultrafiltration membrane of this invention.

Fig. 1B illustrates an alternative apparatus suitable for forming the composite ultrafiltration membrane of this invention.

Fig. 2 is a photomicrograph at 396 x magnification of the cross section of the membrane typical of this invention.

Fig. 3 is a photomicrograph at 1994 x magnification of the cross section of a membrane of Fig. 2 showing the cellulose ultrafiltration layer and its interlocking with the microporous ultra-high-molecular-weight polyethylene substrate.

Fig. 4 is a photomicrograph at 396 x magnification of a membrane of this invention.

Fig. 5 is a photomicrograph at 1060 x magnification of the membrane of Fig. 4.

Fig. 6 is a photomicrograph at 397 x magnification of the membrane of this invention.

Fig. 7 is a photomicrograph at 1002 x magnification of the membrane of Fig. 6.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The defect-free cellulosic membrane of this invention comprises a nonfibrous base resistant polymeric microporous substrate coated with an ultrafiltration layer formed of a cellulose or cellulose ester polymer. A major advantage of the cellulosic membranes of this invention is that they are resistant to degradation by contact with strong alkali solution, such as 0.5N NaOH. The composite membranes of this invention are also resistant to back pressures far exceeding those of the prior art and usually as high as about 100 psi. The bond between the substrate and the ultrafiltration layer can be made sufficiently strong as to exceed the burst strength of the overall membrane. In addition, since the cellulosic ultrafiltration membrane is defect free, the integrity of the ultrafiltration membrane of the invention is substantially superior to the integrity of prior-art composite membranes.

The base resistant microporous polymeric membrane has pore sizes between about 0.05 and 10 microns, preferably between about 0.2 and 1.0 microns. Suitable base resistant microporous membrane substrates are formed from a polyolefin such as polyethylene or polypropylene; polysulfone, polyethersulfone, polyarylsulfone, polytetrafluoroethylene, cellulose or the like. Particularly suitable microporous membrane substrates are formed from ultrahigh molecular weight polyethylene (UHMW-PE) such as those disclosed by U.S. Patents 4,828,772 and 4, 778, 601

which are incorporated herein by reference. A particularly suitable microporous polypropylene membrane substrate is disclosed by U.S. Patent 4,874,567 which is incorporated herein by reference. The base resistant microporous polymeric membrane substrate is not degraded when contacted with a base solution utilized to convert cellulose ester to cellulose.

The ultrafiltration layer is formed from a solution of cellulose or a cellulose ester such as cellulose diacetate, cellulose triacetate, cellulose nitrate or mixtures thereof. After being deposited on the microporous membrane substrate the cellulose ester can be converted to cellulose by reaction with an aqueous basic solution such as NaOH, KOH, LiOH at a pH between about 11.8 and 12.2. The cellulose ester solution is formed with a solvent composition such as acetone, N-methyl pyrrolidone (NMP), dimethylacetamide (DMAC), mixtures thereof or the like.

Coating techniques useful for forming the composite ultrafiltration membrane are disclosed for example by U. S. Patents 5, 017, 292 and 5, 096, 637 which are incorporated herein by reference.

Polymer solutions containing between about 8 and 25 % by weight of the cellulose ester or cellulose polymer in a solvent can be utilized in the present invention. Such solutions can be coated to a dry thickness above the microporous substrate of from about 1 microns to 20 microns, preferably from about 5 to about 15 microns. Controlling the coating thickness within these limits promotes penetration of the coating into the substrate over a distance between about 5 and 30 microns, preferably between about 15 and 25 microns. This results in a cellulosic membrane which can be folded or subjected to moderate or high back pressures without rupturing the cellulosic membrane.

After the cellulose ester polymer solution has been cast onto the microporous membrane, the ultrafiltration membrane structure is formed by immersing the coated microporous structure into a liquid which is miscible with the polymer solvent but is

a non solvent for the dissolved cellulose or cellulose ester polymer. Water is the preferred liquid, although other liquids can be employed such as water-alcohol, water-polymer solvent, water-glycerin mixtures.

Membrane formation occurs by precipitation of the polymer from the polymer solution. The precipitated polymer forms a porous membrane which may or may not be "skinned" or have an asymmetric structure typical of some ultrafiltration membranes but which is substantially defect free. The properties of the membrane can be varied by controlling such parameters as the percent polymer in solution, solvent type, additives, coating thickness, immersion bath composition, immersion bath temperature, etc.

In an aspect of this invention, a hydrophobic microporous base resistant membrane substrate can be modified to render it hydrophilic prior to applying the precursor polymeric solution which forms the ultrafiltration membrane layer. An example of a suitable process is disclosed in U. S. Patent 4,618,553 which is incorporated herein by reference. A membrane having a completely hydrophilic surface is particularly useful when filtering aqueous liquid compositions.

Referring to Fig. 1, coating thickness is controlled by forming a nip between a rotating drum 10 and a non-rotating rubber coated cylinder 12. The microporous substrate 14 can be positioned on an optional support web 18 which contacts the backed drum or roll 10 which can be rotating. The cast polymer solution 28 forms the skin in the final composite membrane of this invention.

In operation, cellulose or a cellulose ester casting solution 20 is fed to a reservoir on the web entry side of the nip point 26 of the rubber covered cylinder 12 and the drum 10. The moving microporous substrate 14 drags solution under the nip 26 analogous to journal bearing lubrication. Coating thickness can then be varied by adjusting the inlet pressure to the pneumatic cylinders 32.

Referring to Fig. 1A, coating thickness is controlled in an alternative apparatus by changing the width of the slot 34, the delivery rate of the polymer solution 30 which is fed to the slot die 12 by means of a suitable positive displacement pump such as a variable speed precision gear pump or the substrate speed. In practice, solution viscosity and casting speed are set primarily by membrane property requirements. The width of the gap 34 is sized based on polymer solution viscosity and thickness of coating (volume) required. The equalization chamber 32 is used to uniformly distribute polymer solution along the entire width of the gap 34.

Referring to Fig. 1B, coating thickness is controlled in a second alternative apparatus by changing the gap 34 between the knife 12 and the substrate 14 to be coated. The coating thickness is also affected by the reservoir height and substrate speed. In practice, the polymer solution is fed to reservoir 30 at a rate which will maintain the solution level in the reservoir constant and the casting (substrate) speed is set primarily by membrane property requirements.

After the membrane structure has formed, the composite web is washed by conveying the coated and precipitated web through a water bath. Contact time of approximately 2 minutes in 25° C water, for example, is sufficient. When initially coating with a cellulose ester solution, the cellulose ester UF composite is then treated with NaOH at high pH to hydrolyze the UF layer. The regenerated cellulose UF composite is then soaked in a humectant solution such as glycerine and water. Drying can then be performed by leaving the rewashed web to dry as single sheets at room temperature. Alternatively, the web can be continuously dried by conveying the web over a heated roll.

The following examples illustrate the present invention and are not intended to limit the same.

Example 1

This example illustrates a process making a 15 kD nominal molecular weight cutoff composite ultrafiltration membrane.

Ultrahigh-molecular-weight polyethylene microporous membrane produced by the process of U.S. Patents 4,778,601 and 4,828,772 having an average pore size of 0.3-0.4 micrometers were employed as the microporous membrane substrate.

A polymer solution containing 20.0 wt% cellulose acetate in 80.0 wt% N-methyl pyrrolidone (NMP) (solvent) was cast onto the microporous polyethylene membrane at a speed of 10 feet per minute utilizing the applicator of Fig. 1 with 45 psi applied pressure. The NMP solvent is not a solvent for the polyethylene substrate. Thus, there is no adhesion between the polyethylene and the cellulose acetate due to solvent bonding. The coated membrane was then immersed in a water bath maintained at a temperature of 30° C. The composite membrane thus produced was subsequently immersed in 0.5N NaOH at 20 °C for 4 hours in order to convert the cellulose acetate to cellulose by hydrolysis. The composite membrane then was washed in water and treated with 20 vol% glycerine in water solution to act as a humectant. It was subsequently dried by conveying the web over a drying roll heated to about 130° F.

The cross-section of the composite membrane produced is shown in Figs 2 and 3. The depth of cellulose infiltration into this polyethylene substrate was approximately 10 microns and the depth of the polyethylene substrate free of cellulose was about 135 microns. The thickness of the cellulose coating above the surface to the UHMW-PE substrate was about 11 microns. The composite membrane was free of defects and had the flux and retention characteristics listed in Table 1.

Example 2

This example illustrates a process making a 110 kD nominal molecular weight cutoff composite ultrafiltration membrane. The method used for Example 2 is the same as in Example 1 with the following exceptions: the polymer solution used was composed of 12.0 wt% cellulose acetate in 88.0 wt% N-methyl pyrrolidone (NMP), the coated membrane was immersed in a water bath maintained at a temperature of 10° C . All other process steps were the same.

The cross-section of the composite membrane produced by Example 2 is shown in Figs 4 and 5. The depth of cellulose infiltration into this polyethylene substrate was approximately 25 microns and the depth of the polyethylene substrate free of cellulose was about 130 microns. The thickness of the cellulose coating above the surface to the UHMW-PE substrate was about 3 microns. The composite membrane was free of defects and had flux and retention characteristics listed in Table 1.

Example 3

This example illustrates a process making a 1,300 kD nominal molecular weight cutoff composite ultrafiltration membrane. The method used for Example 3 is the same as in Example 2 with the following exceptions: the coated membrane was immersed in a water bath maintained at a temperature of 50° C.

The cross-section of the composite membrane produced by Example 3 is shown in Figs 6 and 7. The depth of cellulose infiltration into this polyethylene substrate was approximately 35 microns and the depth of the polyethylene substrate free of cellulose was about 130 microns. The thickness of the cellulose coating above the surface to the UHMW-PE substrate was about 12 microns. Although this membrane clearly contained macrovoids, it was still capable of withstanding high backpressure and had flux and retention characteristics listed in Table 1.

Table 1

Water Flux, 90% Dextran Rejection, Backpressure Capability for Some Cellulose Composite Membranes versus Conventional Membranes

	90% Dextran Rejection kD	Flux, gfd/psi	Water Visual Bubble Point, psig	Reverse Pressure Failure, psig
Example 1	14.7	3.5	>90	> 90**
Example 2	110.0	35.5	>90	> 90**
Example 3	1310	136.2	70 - 90	> 90**
PLAC***	1.5	0.18	>90	< 25
PLGC***	8	1.7	75 - 90	< 20
PLTK***	30	15	5 - 55	< 8
PLHK***	120	45	< 15	< 7
PLMK***	500	90	<10	< 5

** Backpressure test system limitation is 60 psig

***PLAC, PLGC, PLTK, PLHK and PLMK are conventional cellulose ulrafiltration membranes manufactured by Millipore Corporation which utilize a Freudenberg non-woven substrate. Values indicated are typical of these membranes.

WATER FLUX

This test is carried out using a computer controlled automated test system. This system collects data on weight of permeate passing through a test cell as a function of elapsed time. The automated system controls pressure to the inlet of the test cell and temperature of the water. The test pressure for the membranes described was 25 psig and the water temperature was 25 Degrees Celsius. A minimum of 15 grams (ml) of water was collected for each membrane tested. The flux was calculated using the membrane area in the test cell open to the flow path, the volume collected, elapsed time and test pressure.

90% DEXTRAN REJECTION

Rejection of model solutes is the most common method for describing the expected performance of ultrafiltration membranes. Thus, nominal molecular weight limits (NMWL) can be determined with a variety of solutes; frequently proteins are used. The NMWL of a UF membrane is typically the molecular mass of the smallest protein that the membrane rejects at a chosen level, usually 90 to 95%. Other solutes that can be used to characterize UF membranes include dextrans, which are available in a large range of molecular weights. The whole rejection spectrum, from molecules of about 1000 daltons molecular weights to molecules of about 2,000,00 daltons to can be measured in a single test.

The test is based on methods published, inter alia, by L. Zeman and M. Wales, in "Separation Science and Technology" 16 (30), p. 275-290 (1981). The membranes to be characterized are challenged with solutions containing polydisperse dextrans with molecular weights 1000 to 2,000,00 daltons in a suitable device; the permeation rate during the test is controlled at low flux to minimize concentration polarization. Feed and permeate streams are sampled and analyzed by size exclusion chromatography (SEC); the chromatographic data is used to calculate rejection as a function of dextran molecular mass.

Rejection (R) with dextran molecular mass is R=1 - Cp/Cf, where Cp and Cf are the dextran concentrations of given molecular mass in the feed and the permeate, respectively. The molecular weight at which the membrane retains 90% of the dextran feed is the 90% dextran rejection value. Although it is common to call the 90% dextran rejection value a cutoff, care must be taken to distinguish it from cutoffs measured with other solutes such as the solutes used to determine the NMWL.

VISUAL BUBBLE POINT

The visual bubble point test is used to determine the maximum pore size (or defect) of a permeable membrane. The test is based on the fact that liquid is held in the membrane pores by surface tension effects. The minimum pressure required to force liquid out of the pore is a measure of pore diameter as described by the Washburn equation:

$$P = k\,4\,\delta \cos \phi / d$$

where:

P = bubble point pressure

δ = surface tension

ϕ = liquid/solid contact angle

d = pore diameter

k = shape correction factor

ASTM Method 316-80 is employed. In general, this bubble point test is performed by prewetting the filter with the liquid to be used (water for the purposes of this work), increasing the pressure of air up-stream of the filter and watching for bubbles downstream of the filter. The pressure at which a continuous stream of bubbles appears is the visual bubble point.

BACKPRESSURE FAILURE

This test is conducted with a system consisting of a modified 293mm membrane holder (Millipore part number YY3029316), a regulated air pressure source, rotameters to measure air flow (up to 72 cc/min) and miscellaneous valves and tubing. A water wetted membrane is first placed in the test cell. A plastic screen with a 3 mm x 3 mm pattern 0.5mm thick is placed on top of the membrane's ultrafiltration layer. The cell is then closed and sealed. Pressure is applied to the substrate side of the membrane while monitoring both the flow of air upstream from the membrane with rotameters and bubbles formed by the displacement of air downstream of the membrane from a tube inserted into a water filled beaker and connected at the other end to the test cell discharge port. The screen placed in the cell with the membrane allows the ultrafiltration layer to delaminate under the stress of the pressure applied to the substrate side of the membrane. When this occurs, a sharp increase in the flow of air is detected and recorded. The system is designed with a 60 psig maximum pressure capability.

CLAIMS

1. A back-pressure resistant cellulosic ultrafiltration membrane comprising a polymeric microporous base resistant substrate and an ultrafiltration membrane layer formed from a polymer selected from the group consisting of cellulose, a cellulose ester and mixtures thereof said layer having a thickness between about 1 and 20 microns.

2. The cellulosic ultrafiltration membrane of claim 1 wherein said ultrafiltration membrane has a nominal molecular weight cutoff between 500 Daltons and 1,500,000 Daltons.

3. The cellulosic ultrafiltration membrane of claim 1 or 2 wherein said ultrafiltration membrane layer comprises cellulose acetate.

4. The cellulosic ultrafiltration membrane of claim 1 or 2 wherein said ultrafiltration membrane layer comprises cellulose.

5. The cellulosic ultrafiltration membrane of any one of claims 1 or 2 wherein said polymeric microporous base resistant substrate is a polyolefin.

6. The cellulosic ultrafiltration membrane of claim 5 wherein said polyolefin is ultrahigh molecular weight polyethylene.

7. The cellulosic ultrafiltration membrane of claim 6 wherein said ultrafiltration layer comprises cellulose.

8. The cellulosic ultrafiltration membrane of claim 6 wherein said ultrafiltration layer comprises cellulose acetate.

9.. The cellulosic ultrafiltration membrane of claim 5 wherein said polyolefin is polypropylene.

10. The cellulosic ultrafiltration membrane of any one of claims 1 or 2 wherein said polymeric microporous base resistant substrate is selected from the group consisting of polysulfone, polyethersulfone and polyarylsulfone.

11. The cellulosic ultrafiltration membrane of claim 10 wherein said ultrafiltration layer comprises cellulose.

12. The cellulosic ultrafiltration membrane of claim 10 wherein said ultrafiltration layer comprises cellulose acetate.

13. The cellulosic ultrafiltration membrane of claim 9 wherein said ultrafiltration layer comprises cellulose.

14. The cellulosic ultrafiltration membrane of claim 9 wherein said ultrafiltration layer comprises cellulose acetate.

15. The cellulosic ultrafiltration membrane of any one of claims 1 or 2 wherein the entire surface of the membrane substrate is rendered hydrophilic which retains substantially the same porous configuration as the membrane substrate.

16. The cellulosic ultrafiltration membrane of claim 15 wherein said substrate is a polyolefin.

17. The cellulosic ultrafiltration membrane of claim 16 wherein said polyolefin is ultrahigh molecular weight polyethylene.

18. The cellulosic ultrafiltration membrane of claim 16 wherein said polyolefin is polypropylene.

19. The cellulosic ultrafiltration membrane of claim 15 wherein said substrate is selected from the group consisting of polysulfone, polyethersulfone and polyarylsulfone.

20. The cellulosic ultrafiltration membrane of claim 15 wherein the ultrafiltration membrane layer comprises cellulose.

21. The cellulosic ultrafiltration membrane of claim 16 wherein the ultrafiltration membrane layer comprises cellulose.

22. The cellulosic ultrafiltration membrane of claim 17 wherein the ultrafiltration membrane layer comprises cellulose.

23. The cellulosic ultrafiltration membrane of claim 18 wherein the ultrafiltration membrane layer comprises cellulose.

24. The cellulosic ultrafiltration membrane of claim 19 wherein the ultrafiltration membrane layer comprises cellulose.

25. The cellulosic ultrafiltration membrane of claim 15 wherein the ultrafiltration membrane layer comprises cellulose ester.

26. The cellulosic ultrafiltration membrane of claim 16 wherein the ultrafiltration membrane layer comprises cellulose ester.

27. The cellulosic ultrafiltration membrane of claim 17 wherein the ultrafiltration membrane layer comprises cellulose ester.

28. The cellulosic ultrafiltration membrane of claim 18 wherein the ultrafiltration membrane layer comprises cellulose ester.

29. The cellulosic ultrafiltration membrane of claim 19 wherein the ultrafiltration membrane layer comprises cellulose ester.

30. The cellulosic ultrafiltration membrane of claim 15 wherein the ultrafiltration membrane layer comprises cellulose ester.

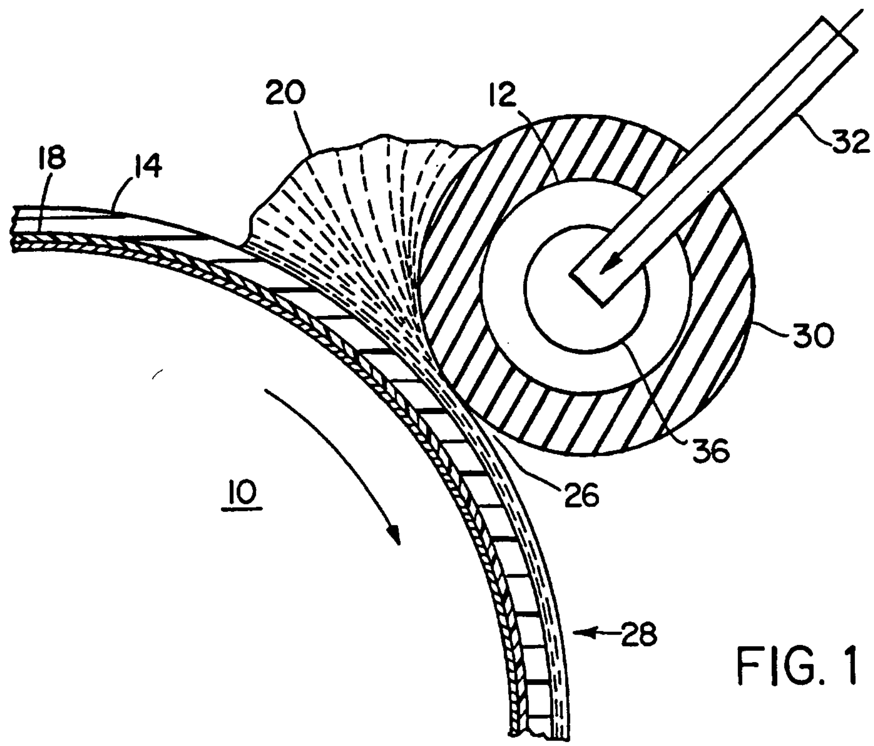


FIG. 1

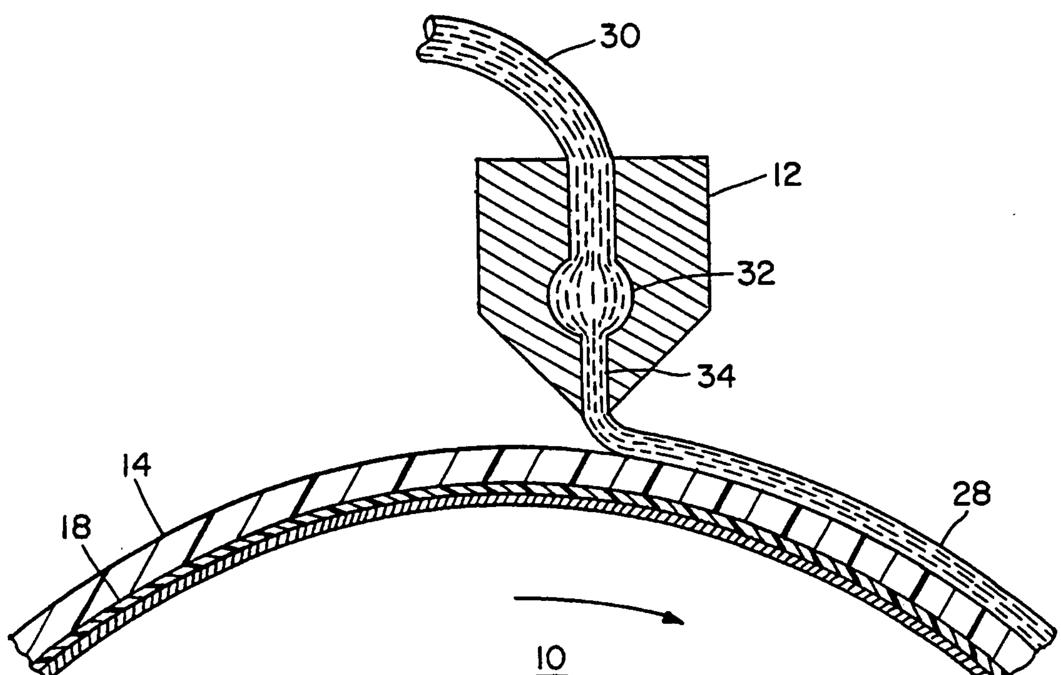


FIG. 1A

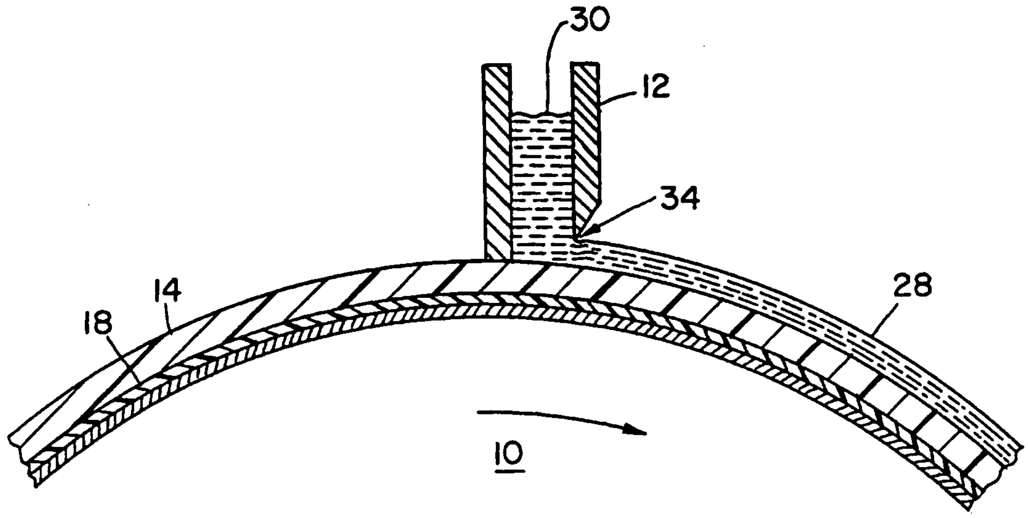


FIG. 1B

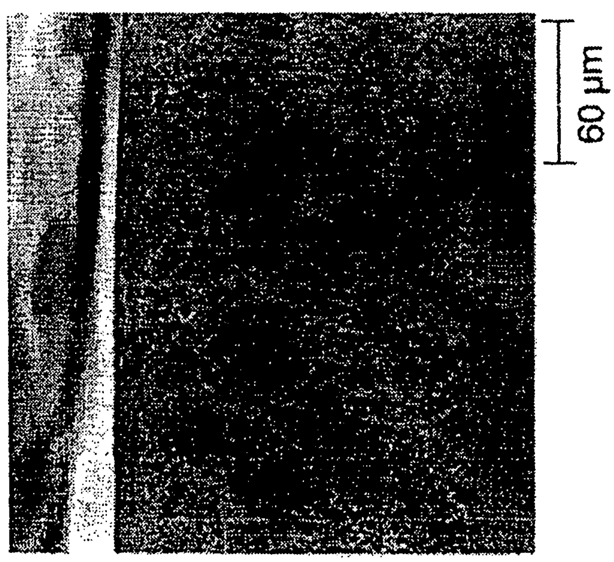


FIG. 2

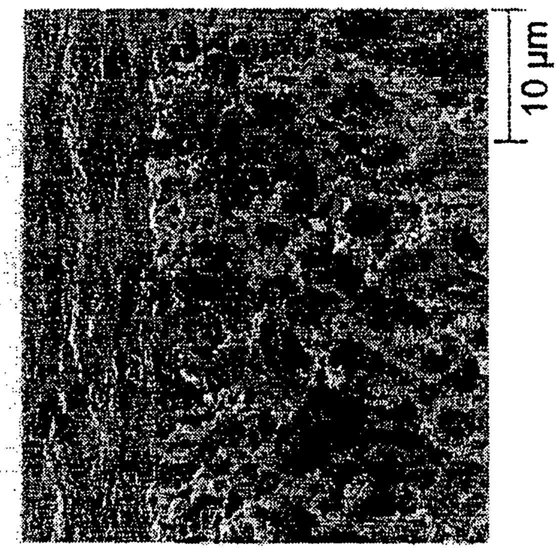


FIG. 3

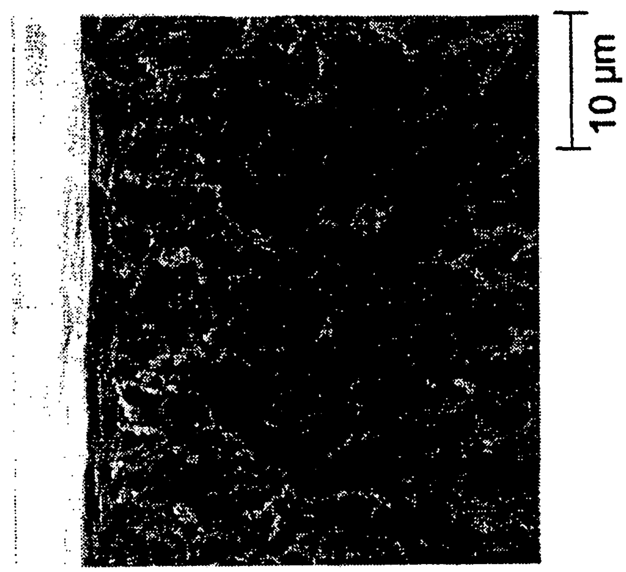


FIG. 5

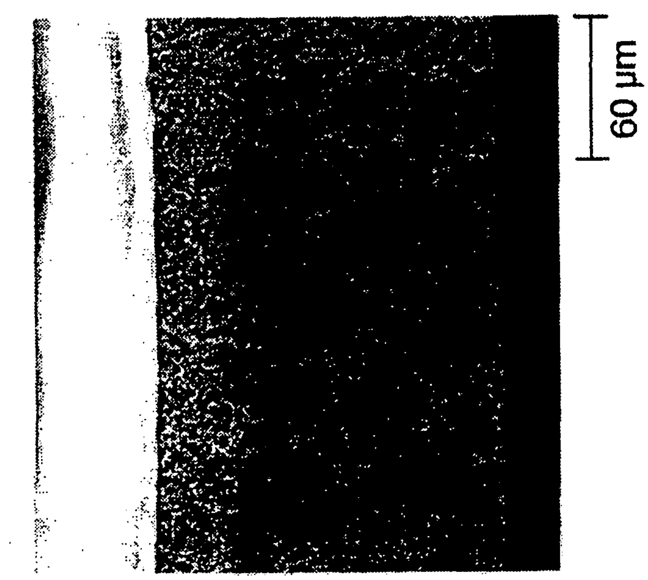


FIG. 4

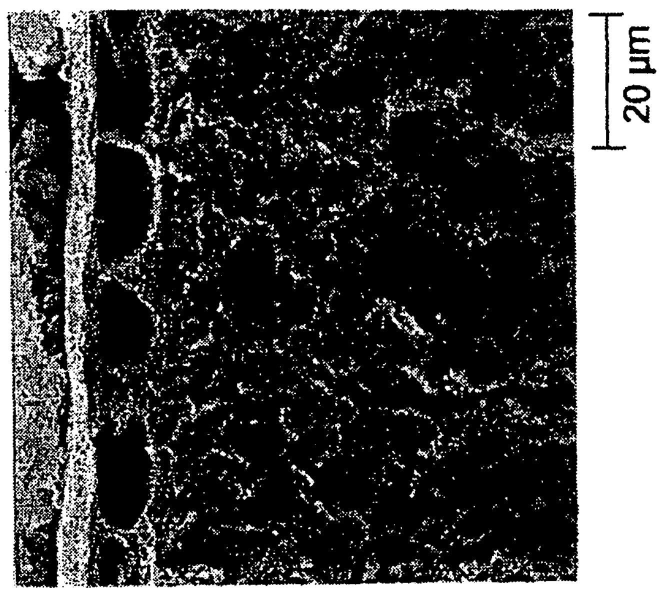


FIG. 7

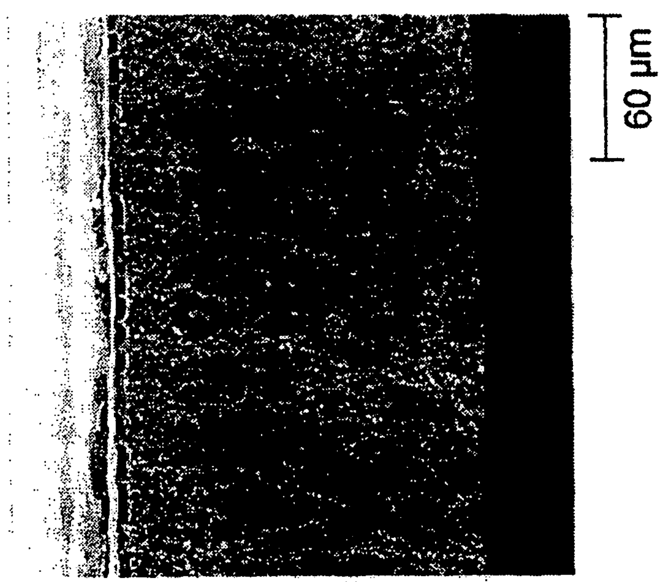


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/09836

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D71/10 B01D71/14 B01D69/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 498 348 (JAPAN GORE-TEX, INC.) 12 August 1992 see the whole document ---	1,3,15
A	FR,A,2 488 051 (CELANESE CORP.) 5 February 1982 see the whole document ---	1,3,15
A	EP,A,0 096 339 (GTF INGENIEURBURO FUR INDUSTRIEANLAGENBAU) 21 December 1983 see the whole document ---	1,3
A	US,A,4 978 451 (JOHN A. TAYLOR) 18 December 1990 see the whole document ---	1,4
A	FR,A,2 380 052 (AKZO NV) 8 September 1978 see the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 November 1995	29.11.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Devisme, F

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 95/09836

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-498348	12-08-92	DE-D-	69201890	11-05-95
		DE-T-	69201890	03-08-95
		US-A-	5445739	29-08-95
FR-A-2488051	05-02-82	US-A-	4359510	16-11-82
		CA-A-	1169118	12-06-84
		DE-A-	3130069	04-03-82
		GB-A,B	2081604	24-02-82
		JP-B-	6019980	16-03-94
		JP-A-	57055064	01-04-82
		US-A-	4438185	20-03-84
EP-A-96339	21-12-83	DE-A-	3220570	01-12-83
		DE-A-	3378677	19-01-89
		JP-C-	1679988	13-07-92
		JP-B-	3034969	24-05-91
		JP-A-	59109204	23-06-84
		US-A-	4915834	10-04-90
		US-A-	5156740	20-10-92
		US-A-	4755299	05-07-88
US-A-4978451	18-12-90	AU-B-	623946	28-05-92
		AU-B-	4547089	20-06-91
		CA-A-	2007799	05-03-91
		CN-A-	1049980	20-03-91
		EP-A-	0418432	27-03-91
		JP-A-	3098623	24-04-91
FR-A-2380052	08-09-78	DE-A-	2705733	17-08-78
		DE-A-	2705735	17-08-78
		AT-B-	371341	27-06-83
		BE-A-	863833	29-05-78
		GB-A-	1562069	05-03-80
		JP-C-	1198260	21-03-84
		JP-A-	53100698	02-09-78
		JP-B-	57035018	27-07-82
		US-A-	4276172	30-06-81